

# Supporting information to:

## *Reduction of a Ni/Spinel Catalyst for Methane Reforming*

Jan Kehres,<sup>a</sup> Jens Wenzel Andreasen,<sup>b\*</sup> Jostein Bø Fløystad,<sup>c</sup> Haihua Liu,<sup>d</sup>  
Alfons Molenbroek,<sup>e</sup> Jon Geest Jakobsen,<sup>e</sup> Ib Chorkendorff,<sup>a</sup> Jane Hvolbæk  
Nielsen,<sup>a</sup> Kristin Høydalsvik,<sup>c</sup> Dag Werner Breiby,<sup>c</sup> and Tejs Vegge<sup>b</sup>

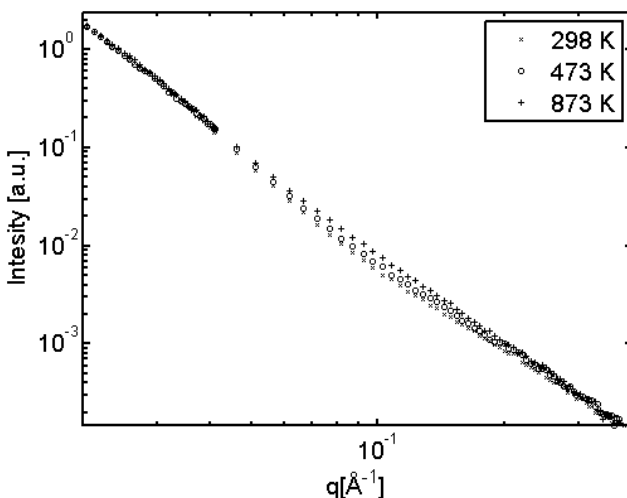
<sup>a</sup> Center for Individual Nanoparticle Functionality, Department of Physics, Technical University of Denmark, Kgs. Lyngby, Denmark, <sup>b</sup> Department of Energy Conversion and Storage, Technical University of Denmark, Roskilde, Denmark, <sup>c</sup> Department of Physics, Norwegian University of Science and Technology, Trondheim, Norway, <sup>d</sup> Physical Biology Center for Ultrafast Science and Technology, Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, USA, <sup>e</sup> Haldor Topsøe A/S, Kgs. Lyngby, Denmark

E-mail: [jewa@dtu.dk](mailto:jewa@dtu.dk)

## *In situ* SAXS

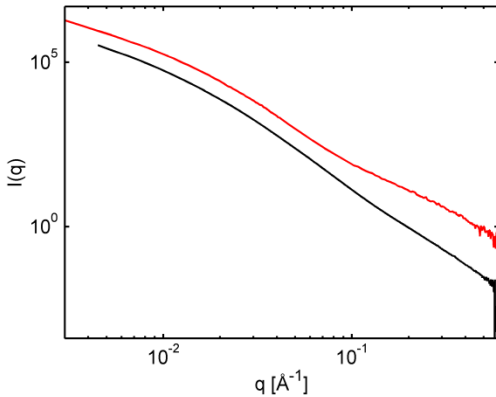
The *in situ* SAXS of the Ni/MgAl<sub>2</sub>O<sub>4</sub> catalyst was acquired simultaneously with the WAXS in the pinhole laboratory camera. SAXS was acquired with a 2D “Gabriel” type gas detector [1] in two different sample to detector distances of 1494 mm (short geometry) and 4679 mm (long geometry) covering a  $q$ -range of  $0.002 < q < 0.45 \text{ \AA}^{-1}$  by using Mo K-alpha  $\lambda = 0.7107 \text{ \AA}$  in the short and Cu K-alpha radiation  $\lambda = 1.5418 \text{ \AA}$  in the long geometry. The 2D SAXS data, acquired in both geometries during the *in situ* reduction were azimuthally averaged using the Fit2d software package from ESRF [2]. After background subtraction, the data were scaled to interpolate intensities in the overlapping angular region, calculating the quotient for the individual data points and using the mean to determine a scaling factor.

The SAXS acquired with the laboratory pinhole camera showed changes in the  $q$ -range where the Ni/NiO-particles contribute to the pattern in a similar temperature range where the reduction of NiO was observed with WAXS.



**S1:** SAXS data at intermediate  $q$  at 298 K (x), first pattern at 473 K (o) and last pattern at 873 K (+).

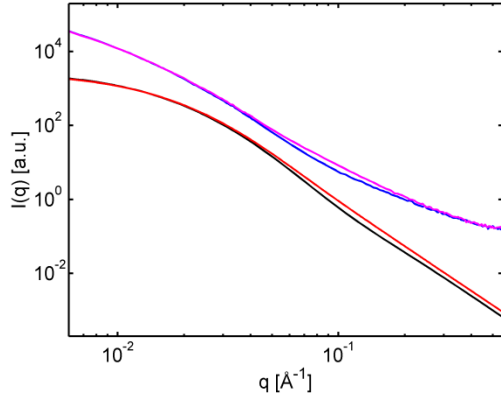
However, a complete analysis of the acquired SAXS during the reduction of the Ni/MgAl<sub>2</sub>O<sub>4</sub> catalyst in the laboratory setup was not possible. The 1D-transformed and background subtracted data, acquired with Mo-K<sub>α</sub> radiation in short geometry, shows a significantly different trend at higher  $q$  than the data acquired at the B1 beamline at HASYLAB. In fact the observed artifact showed similarities with the knee like Guinier regime observed with Cu- K<sub>α</sub> radiation in long geometry at low  $q$ , see S2. The origin of this artifact has not been understood yet. However, it occurred reproducibly and only when using Mo-K<sub>α</sub> radiation and even after complete realignment of the SAXS camera, including the X-ray optics. One conceivable explanation may be contamination of the monochromatic beam with photons of a longer wavelength, possibly by total reflection of lower energy photons of the Mo bremsstrahlung spectrum on the X-ray multilayer optics.



**S2: overlapped SAXS acquired in long geometry with Cu-K $\alpha$  and in short geometry with Mo-K $\alpha$  radiation (red) and at the B1 beamline at HASYLAB (black).**

Comparing the scattering cross section for the Ni/NiO and the reduced Ni particle, simulated using the parameters obtained from the least square fit from the ASAXS data, shows however

clearly that the changes observed in the SAXS acquired in the laboratory setup can be attributed to the reduction of the NiO shell, see S3.



**S3: Overlapped SAXS of a fresh (blue) and reduced (magenta)  $w(\text{Ni}) = 22\text{wt}\%$  Ni/MgAl<sub>2</sub>O<sub>4</sub> catalyst, acquired in the laboratory setup and simulated scattering cross section using the parameters obtained from a least square fit of the ASAXS data for a Ni/NiO core shell particle (black) and a pure Ni particle (red). Note, the SAXS acquired in short geometry using Mo-K <sub>$\alpha$</sub>  radiation is not background corrected.**

### ASAXS analysis

The separation of the small angle scattering cross section from the patterns recorded at several energies  $I(q, E_i)$  can be compared with solving a set of linear equations. If we define an  $m \times n$  matrix of small angle scattering intensities  $\mathbf{I}$  at  $m$  scattering vectors  $q$ , measured at  $n$  energies, an  $n \times k$  matrix of scattering contrasts of  $k$  self- or cross-correlations  $\mathbf{D}$ , and an  $m \times k$  matrix of structure functions  $\mathbf{F}$  we obtain  $\mathbf{FD}^T = \mathbf{I}$ . Owing to measurement uncertainties this is a least square problem which, depending on the number of components and measurement energies, may be under- or overdetermined. Any real  $m \times n$  matrix  $\mathbf{A}$  can be decomposed:<sup>3</sup>

$$\mathbf{A} = \mathbf{U}\mathbf{S}\mathbf{V}^T \quad (1)$$

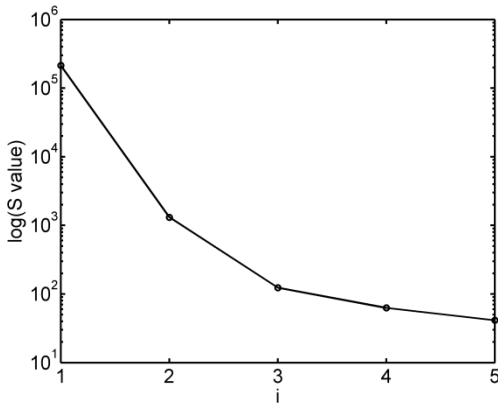
where  $\mathbf{U}$  and  $\mathbf{V}$  are orthogonal matrices of the left and right singular vectors of  $\mathbf{A}$ , and  $\mathbf{S}$  is a diagonal matrix containing the singular values, ranked from the greatest to the least. The ‘effective rank’ of the matrix decomposition provides information about the number of independent basis vectors describing the system of equations. The pseudo inverse  $\mathbf{A}^+$  can be formed from the products of the decomposition

$$\mathbf{A}^+ = \mathbf{U}\mathbf{S}^+\mathbf{U}^T \quad (2)$$

and the least square solution with the smallest norm of a system of linear equations  $\mathbf{A}\mathbf{X} = \mathbf{B}$  can be obtained from

$$\mathbf{X} = \mathbf{A}^+\mathbf{B} \quad (3)$$

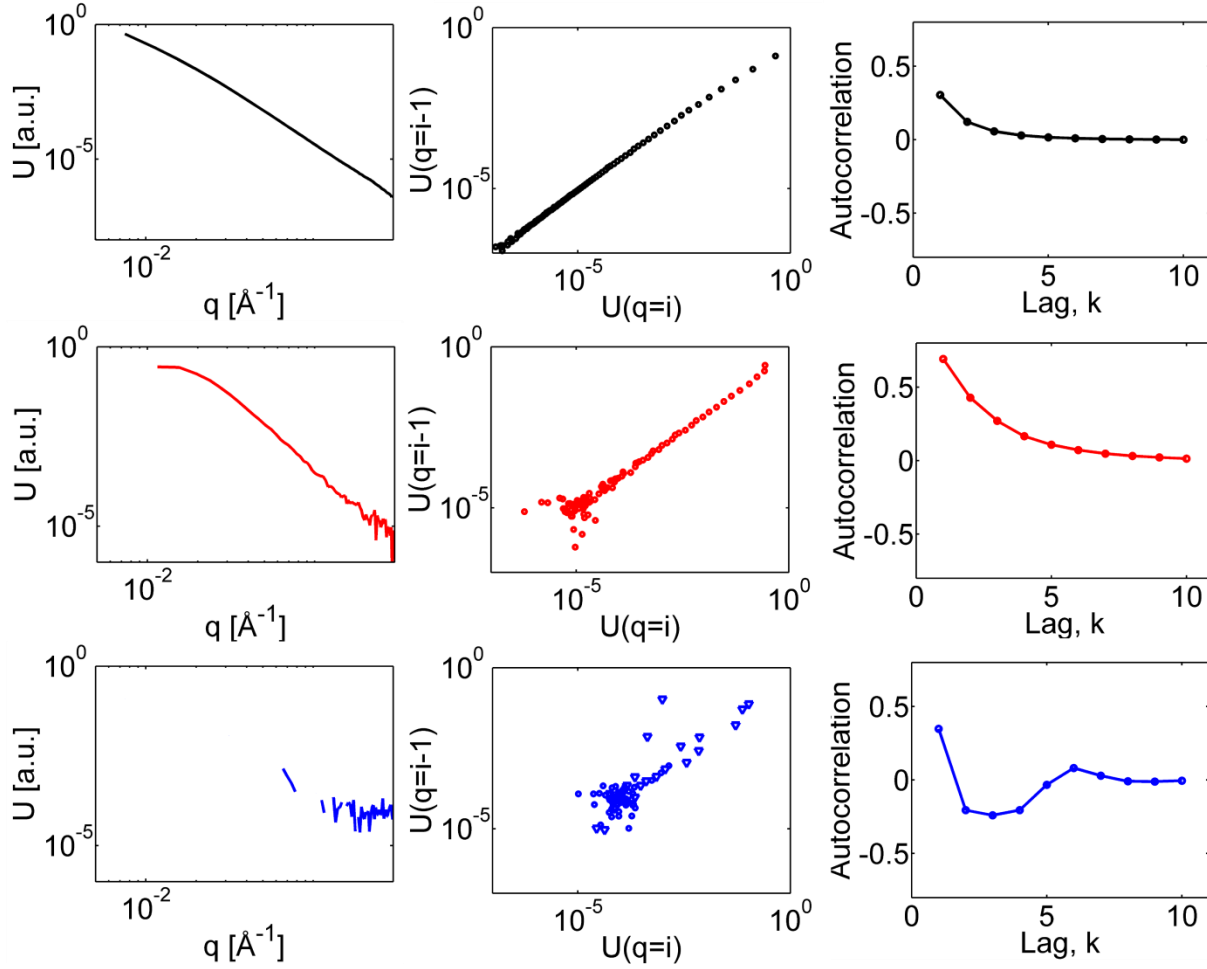
The singular values of the matrix decomposition of  $\mathbf{I}$  for the catalyst prior to reduction are shown in figure S4.



**S4: Singular values for the five scattering cross section measured below the Ni-K-absorption edge for the catalyst prior to reduction.**

From a visual inspection of the singular values alone it was not possible to unequivocally define the rank of system and thereby the number of significant electron density contrasts required to

solve the set of linear equations. Therefore the basis vectors of the decomposition were inspected separately.



**S5: The first three basis vectors of  $U$  obtained from the singular value decomposition (left column) and corresponding lag-plot,  $Y_i$  versus  $Y_{i-1}$  (middle column), negative values are indicated by triangles, and plot of the autocorrelation function (right column) for the catalyst prior to reduction.**

A plot of the first two basis vectors indicates that they actually resemble small angle scattering cross sections, whereas the third basis vector is largely randomly distributed around zero (see left column S5). The same is indicated by lag-plots ( $Y_i$  versus  $Y_{i-1}$ ) and plots of the autocorrelation

function versus lag (middle and right column). The lag-plots of the first two basis vectors show strong serial correlation, which would be expected for a small angle scattering cross section, whereas the lag-plot of the third basis vector looks nearly random (see middle column S5). The autocorrelation function for the first basis vectors decreases monotonic as we would expect for a small angle scattering cross section, whereas the autocorrelation function of the third basis vector is non-monotonic. The rank of the system has been therefore estimated to be two, i.e. two relevant scattering contrasts are required for solving the set of equations.

The first basis vector, separated by singular value decomposition, follows closely the total scattering curve. Since the  $\text{MgAl}_2\text{O}_4$  particles are expected to be large compared to the Ni catalyst particles, we assume the total scattering curve to be dominated by scattering of the support. The first basis vector is therefore assumed to represent the contribution of  $\text{MgAl}_2\text{O}_4$  support particles to the total scattering. The second basis was assumed to represent the scattering contributions of the Ni/NiO catalyst particles. The absence of a third relevant basis vector indicates for us that the Ni- $\text{MgAl}_2\text{O}_4$  cross term can be neglected for separation of the Ni small angle scattering cross section from the patterns acquired at 5 energies below the Ni-k-edge.

The system of equations was therefore solved considering the relevant scattering contrasts for

$$|\Delta\rho_{\text{MgAl}_2\text{O}_4}| = \text{Re}(\rho_{\text{MgAl}_2\text{O}_4})^2 + \text{Im}(\rho_{\text{MgAl}_2\text{O}_4})^2 \quad (4)$$

$$|\Delta\rho_{\text{Ni}}| = \text{Re}(\rho_{\text{Ni}})^2 + \text{Im}(\rho_{\text{Ni}})^2 \quad (5)$$

The separated scattering contribution was derived by multiplication of the pseudo inverse of the scattering contrasts matrix  $\mathbf{D}^+$ , constructed considering the energy dependent relevant scattering contrasts of  $\text{MgAl}_2\text{O}_4$  and Ni, with the matrix of small angle scattering intensities  $\mathbf{I}$  acquired at the 5 energies below the Ni-K-absorption edge,  $\mathbf{F} = \mathbf{D}^+\mathbf{I}$ .

The procedure was similarly applied to derive the scattering contributions of the Ni particles for the reduced catalyst.

## References

1. Gabriel, F.; Dauvergne F.; Rosenbaum, G. Linear, Circular and Two Dimensional Position Sensitive Detectors *Nucl. Instrum. Methods* **1978**, *152*, 191 – 194.
2. Hammersley, A. P. *Internal Report ESRF97HA02T*; ESRF: Grenoble, France 1997.
3. Golub, G. H.; Reinsch, C. Singular Value Decomposition and Least Squares Solutions *Numer. Math.* **1970**, *14*, 403 – 420.